











BULK PHASE AND CHEMICAL COMPOSITION ANALYSIS OF TWO 19TH CENTURY RUSSIAN PLATINUM COINS BY NEUTRON AND COMPLEMENTARY METHODS

19. SZÁZADI OROSZ PLATINAÉRMÉK TÉRFOGATI FÁZIS ÉS KÉMIAI ÖSSZETÉTEL VIZSGÁLATA NEUTRONOS ÉS KIEGÉSZÍTŐ MÓDSZEREKKEL

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Abstract

The composition of early 19th century platinum coins reflects the advances of platinum metallurgy from laboratory-scale refining to industrial-scale processing. An array of neutron methods was used to determine for the first time the bulk phase and elemental composition of two coins, dated 1837 and 1838. Neutron imaging confirmed the homogenous internal structure of the metal at the micrometer scale, with further support from small-angle neutron scattering at the nanometre scale. Prompt gamma activation analysis showed the coins to consist of technically pure platinum, appropriate for the time of their production with iridium and iron between 1 and 2 weight percent. Lower amounts of copper, rhodium, manganese and gold were also detected in the range of tens to thousands of µg/g. Overall, the investigation demonstrated the suitability of neutron methods as non-invasive and reliable bulk means to determine the composition of early industrial platinum to track the development of refining processes and metallurgical processing.

Kivonat

A 19. század elejéről származó platinaérmék összetétele tükrözi a platinakohászat fejlődését a laboratóriumi méretű finomítástól az ipari méretű feldolgozásig. Tanulmányunkban két, 1837-ből és 1838-ból származó érmén végzett első neutronos vizsgálatok térfogati fázis- és elemi összetétel eredményeit mutatjuk be. A neutronos képalkotás megerősítette, hogy a fém belső szerkezete mikrométeres skálán homogénnek tekinthető. Ezt az eredményt tovább erősítették a kismögű neutronszórás eredményei, melyek nanométeres léptékben igazolták ugyanezt. Prompt gamma aktivációs analízissel meghatároztuk, hogy az érmék tiszta platinából állnak 1–2 tömegszázalékos irídium és vastartalommal, amely jellemző a gyártásuk időszakára. Az érmékben ezen kívül kisebb, tíztől ezer µg/g-os mennyiségben mutattunk ki rezet, ródiomot, mangánt és aranyat. Vizsgálataink igazolták, hogy a neutronos módszerek teljesen roncsolásmentes módon adnak megbízható eredményeket a korai ipari platina térfogati összetételéről, ezen túlmenően a finomítás és a kohászati eljárások fejlődésének nyomon követésére is alkalmasak.

KEYWORDS: NON-DESTRUCTIVE ANALYSIS, PLATINUM COIN, SANS, PGAA, ToF-ND, PIXE

KULCSSZAVAK: RONCSOLÁSMENTES VIZSGÁLAT, PLATINA ÉRME, SANS, PGAA, ToF-ND, PIXE

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Introduction

During the first half of the 19th century, platinum refining and processing made major progress and evolved from a small-scale though profitable laboratory-based niche technology (Wollaston 1829) to a scale sufficient to sustain nearly two decades of routine coin production (Sobolewsky 1835), totalling nearly 50 tons of metal (McDonald & Hunt 1982). In a climate of intense academic competition in fundamental research into platinum chemistry and the associated commercialisation of platinum metal production few contemporary reports exist detailing the research and development conducted at the different research centres of the time (Schneider 1868). In particular, issues of quality control and consistency of operation are not documented on a level sufficient to trace incremental progress in the operations, or the implementation of specific innovations even where they are mentioned in the literature. A series of papers using primarily X-ray methods on a set of seven Russian 3-Rouble coins dated from 1828 through to 1842 provided an initial framework to identify these well-dated issues as the most promising and unbiased material archive of the development of platinum metallurgy during the critical period in the first half of the 19th century AD (Auer et al. 1998; Rehren 2006). To trace the technical development on a scale sufficient to be representative for the metal production for each year, and to identify the potential effects of the reported modifications in the production process would require a much larger set of coins to be studied, to understand the consistency in composition within each year's issue, and then among the different issues as time progressed. Also, the analyses need to be non-invasive and without the distorting effects of intentional surface modification, such as stamping and pickling as part of the production process, and the subsequent alterations through wear and tear.

Neutron methods are uniquely suited to determine key physical and chemical aspects of objects without the need for invasive sampling, and without being limited to the surface only, even for such challenging materials as metallic platinum. This pilot study examined the utility of a range of neutron methods to address research questions related to the development of platinum metallurgy at the Royal Mint of St Petersburg in Russia, which spearheaded the development of platinum refining and processing from the laboratory scale of western chemists to a routine large-scale operation. Targeted research used prompt gamma activation analysis (PGAA) to determine the bulk composition of two coins, complemented by particle-induced X-ray emission (PIXE) to correlate surface composition to bulk composition. High resolution time-of-flight neutron diffraction (ToF-ND) was used to determine the phase composition of the coins, focussing

on the presence of a few volume percent of iron oxides and possible shifts in the cell parameters of the platinum matrix as a result of the presence of alloying components in the metal. Neutron imaging was performed to ascertain the coarse-grain (>100 μm) homogeneity of the coins' interior, and small-angle neutron scattering (SANS) was used to explore the homogeneity of the metal matrix on the nanoscale, confirming or contradicting the existence of nanometric-size second phases or precipitates, as well as the texture orientation of the coins.

Two coins of the original set studied in the 1990s and early 2000s were available for this pilot study. Issued in 1837 and 1838, respectively, they weighed just over 10 grams each with a density of just over 20 g/cm^3 and showed a noticeable magnetic response to a hand-held magnet, indicating the presence of a significant iron compound (Auer et al. 1998). They had been thoroughly studied before using primarily X-ray based methods (wavelength-dispersive and energy-dispersive X-ray Fluorescence spectrometry, X-ray Diffraction). These methods indicated that the coins consisted of technically pure platinum metal (96 to 98 wt%) with impurities of iron and iridium in the order of 1 to 2 wt% each, and lower impurities of a wide range of PGEs and transition metals (Rehren et al. 2012). This was further supported by invasive metallography for a single coin (1837), identifying the presence of various iron oxide inclusions throughout the matrix of that coin but not near the surface, probably due to the pickling of the metal discs prior to striking (Weerd et al. 2004). These investigations demonstrated the real potential of compositional and phase analysis of these coins, while emphasising the necessity to apply whole-body analyses rather than being restricted to surface-only approaches.

Materials and methods

PGAA and off-line counting measurements

Prompt gamma activation analysis (PGAA, Révay & Belgya 2004) (**Fig. 1.**) is a non-destructive nuclear analytical technique to determine elemental compositions (Révay 2009). It has been previously applied mostly in provenance or technological studies to characterise heritage objects made of stone (Kasztovszky et al. 2022) and glass (Moropoulou et al. 2016). PGAA proved to be successful in the analysis of alloys (Kiss et al. 2015) even with micro- and macroscopic heterogeneities (Tarbay et al. 2021). The main benefit of PGAA is that due to the highly penetrating properties of neutrons and gamma photons, its results represent the entire irradiated volume instead of only the near-surface volume. Therefore, it was chosen to determine the true bulk chemical composition of the coins unaffected by surface treatments.

During analysis, the whole coin was irradiated in a cold (i.e. low energy) neutron beam and the gamma-rays from the radiative capture were detected. In most cases, major components and a few significant trace elements can be quantified from one spectrum. Elements have fingerprint-like prompt gamma spectra with gamma peaks of 50 keV–10 MeV energy. In principle every chemical element (except He) can be detected with the standard PGAA set-up that includes a high-purity germanium detector. Due to their more complicated spectra, elements with higher atomic number ($Z > 30$, except for Sn and Pb) can be analyzed more precisely using a low-energy germanium detector (LEGe) with superior energy resolution (Maróti et al. 2016), since these elements have their strongest peaks in the low energy region. During the neutron irradiation of the prompt gamma measurements, short and medium half-life radioactive nuclides might form. Thus, PGAA can be complemented with a subsequent series of off-line counting measurements to improve detection of minor impurities within the platinum matrix – if these have short or medium half-life nuclides. This method is called in-beam activation analysis (Szentmiklósi et al. 2008; Révay et al. 2015). The PGAA measurements were carried out at the NIPS-NORMA station (**Fig. 1c.**) of the Budapest Neutron Centre (Szentmiklósi et al. 2010; Szentmiklósi et al. 2013; Kis et al. 2015) using a Compton-suppressed LEGe detector (Maróti et al. 2016), which was successfully applied earlier on a large set of silver coins (Šmit et al. 2020). The intensity of the neutron beam, characterized by the thermal equivalent flux, was $2.7 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$, the cross section of the neutron beam was set to $10 \times 13 \text{ mm}$, thus, almost the entire coin volumes were irradiated.

The gamma-ray spectra were evaluated using the Hypermet-PC program. The spectroscopic data library used in the analysis was established earlier at the Centre for Energy Research (Révay & Molnár 2003; Révay et al. 2004). As the data library contains the first 42 most intense platinum prompt gamma peaks down to about 1% relative intensity, a pure (99.97) platinum foil was analysed immediately after the two coins to detect its weaker prompt gamma peaks. For the detection of elements with lower cross section in the platinum matrix, these peaks need to be adequately corrected for. The compositions of the analysed samples were determined using the methods described in Révay (2009), while the uncertainties of the concentrations were calculated according to Révay (2006).

The off-line counting measurements were carried out in a low-background chamber (Kis et al. 2013) using an unsuppressed 13% HPGe detector (**Fig. 1d.**). The calculation of concentrations relied on the existing k_0 database (Jaćimović et al. 2014; <https://www.kayzero.com/k0naa/k0naaorg/k0->

[ISC.html](#)), a different set of nuclear data (Farina Arboccó et al. 2014) as well as on the general formulae of INAA simplified to subthermal activation, containing the saturation, decay and counting factors, described in more detail in Szentmiklósi et al. (2008) and Révay et al. (2015).

PIXE

External milli-beam particle induced X-ray emission spectroscopy (PIXE) is successfully used for non-invasive elemental surface analysis (Gyódi et al. 1999). The characteristic X-rays produced by the interaction of the incident proton beam with the material at the selected surface area are used for quantitative analysis of the irradiated volume. Due to the deceleration of the incident protons in the sample and the attenuation of the out-coming X-rays the method is inherently sensitive only for a near-surface region of depths up to some tens of micrometres, depending on the composition of the sample, the primary proton energy and the energy of the characteristic X-rays. The ultra-heavy matrix of the coins analysed here limited the analytical depth to a few micrometers. We chose to use this method in order to compare the surface composition to the bulk composition; any systematic differences are likely the result of the intentional surface pickling of the coin blanks and thus bear information on the final step of the coin production. Furthermore, the comparison between bulk and surface composition would indicate whether neutron methods are really necessary for the research question in hand.

In standard detection arrangement elements from Al to U can be detected simultaneously, in favourable conditions down to mg/g sensitivities (Johansson et al. 1995). Our PIXE measurements were performed at the 5 MV Van de Graaf accelerator of the HUN-REN Wigner Research Centre, Institute of Particle and Nuclear Physics. A closely collimated proton beam of 2.5 MeV energy was extracted from the evacuated beam pipe to air through a 7.5 μm thick Kapton foil. A target-window distance of 10 mm was chosen for the measurements at which point the beam diameter was found to be about 1.5 mm, using an external beam current in the range of 1–10 nA.

The PIXE measurements were done on the reverse side of the coin as well as on the cross section of the cut rubel (see **Fig. 1a-b.**). The characteristic X-ray spectra were recorded by a computer controlled Amptek X-123 spectrometer with an SDD type detector of $25 \text{ mm}^2 \times 500 \mu\text{m}$ active volume positioned at 135° to the beam direction. The energy resolution was 130 eV for the Mn Ka line. The net X-ray peak intensities were calculated into element concentrations using the off-line GUPIX program package (Campbell et al. 2000).



Fig. 1: Experiment photos. **a-b** Using PIXE the middle part of both platinum coins and the cut inner surface was analysed with a 1.5 mm diameter beam. **c** During the PGAA measurements, nearly the entire volume was irradiated in the NIPS-NORMA sample chamber. **d** The off-line counting measurements after the neutron irradiation took place at the low-background chamber.

1. ábra: Az alkalmazott kísérleti berendezések. **a-b** PIXE módszerrel az érmék külső felszínének közepén, illetve az érmék vágott keresztmetszetén végeztünk méréseket. **c** A NIPS-NORMA mintakamrában elvégzett PGAA mérések során az érmék közel teljes térfogatát besugarazzuk. **d** A méréseket követő off-line gamma spektrometriára a mérőhely mellett található alacsony háttérű mérőkamrában került sor.

ToF-ND

The ToF-ND at the Budapest Neutron Centre is a high-resolution time-of-flight neutron diffractometer capable of analyzing lattice parameters within the bulk of a heavy metal object. We used this specifically to determine the mineralogical nature of the iron oxide inclusions, and to determine potential cell parameter shifts of the platinum matrix as a result of the unintentional alloying of the metal with residual impurities from the refining process.

The fast double choppers of the ToF-ND instrument can produce neutron pulses as short as 10 ms; the total flight path of neutrons to the detectors is 25 m. In the highest resolution mode and back scattering geometry diffraction spectra with peak widths of 1.5×10^{-3} Å can be collected. The data acquisition consists of an event recorder registering all events

(neutron capture, chopper signs and any external signal) together with a time stamp to a file. This method facilitated recording Bragg-diffraction peaks, i.e. the angular distributions of grains' orientations, thus separating larger crystallites from powder-like phases. The instrument is generally used to investigate much larger samples; to increase sensitivity in this case we applied very long measuring times, so that the detectable absolute mass of iron oxides was as low as about 10 mg, i.e. less than 0.1% of the measured sample mass.

SANS

Small-angle neutron scattering was used for the nanoscale structural analysis of the coins. The SANS method provides information about the nanoscale inhomogeneities, averaged over the whole measured volume. From the neutron scattering perspective, an inhomogeneity (also referred to

as a scattering domain) is a nanosized region of the material whose neutron scattering length density differs from that of its surrounding matrix. SANS yields insight into the size, shape, and surface characteristics of these scattering domains in a non-destructive way.

In a SANS experiment the neutrons scattered elastically and coherently in angles smaller than 10 degrees are collected by a two-dimensional (2D) neutron detector.

The neutron intensity is recorded as a function of the scattering vector Q , which is defined as the difference between the wave vectors of the incident and scattered neutrons, and is given by Equation 1

$$Q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad \text{Eq. 1}$$

where λ is the wavelength of the monochromatic neutron beam, and θ is the scattering angle.

The 2D scattering patterns recorded by the detector may appear symmetric around the center of the neutron beam (isotropic scattering) or exhibit asymmetry, indicating that the structural properties of the sample vary along different directions (anisotropy) (see section ‘Nanostructure’).

In isotropic cases, the recorded neutron intensity is radially averaged, and after the appropriate calibration routine, an intensity versus Q curve is generated (see section ‘Nanostructure’). The shape of this curve will provide adequate information about the nanoscale structure of the sample. The quantitative evaluation of the one-dimensional SANS curves is made by the least-square model fitting method (Len et al. 2022).

The measurements were performed at the YS-SANS instrument of the Budapest Neutron Centre (Len & Almásy 2019). The used sample-to-detector distances were 1.13 m and 5.25 m, and the used wavelengths were 4.4 Å and 8.6 Å. The samples were placed in the beam as received.

Both coins showed anisotropy at the largest measured Q range (see section ‘Nanostructure’). As the anisotropy was only perceived at the high Q range, the overall data evaluation was done in 1D. The radially averaged curve’s middle and high Q range parts were model fitted with the aid of the power-law model, which is used for shape-independent scattering domains (Len et al. 2022).

Neutron Radiography

Neutron radiography (NR) is based on the attenuation of a neutron beam prior to its recording on a 2-dimensional screen. It is a direct imaging technique, where the visual representation of an object is obtained by detecting the modification of the incident beam as it passes through the matter (Banhart 2008; Anderson et al. 2009). The inter-

actions between the radiation and the object determine the contrast, revealing the internal structure of the sample. Here, we used NR in order to test whether there are compositionally distinct particles trapped within the matrix of the coins which would indicate a potential by-passing of the laborious refining process for some of the raw platinum ore, or other fraudulent adulteration of the metal.

A setup called NORMA was installed at the Budapest Neutron Centre as a part of the NIPS experimental station in 2011 (Szentmiklósi et al. 2013; Kis et al. 2015), where the thermal equivalent flux of the guided cold neutron beam is about $2.7 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ and the cross-sectional area of the neutron beam, i.e. the maximum area to capture an image is $43 \times 43 \text{ mm}^2$. The coins were positioned immediately in front of the screen downstream of the neutron collimators, and the transmitted neutrons created signals in a two-dimensional position sensitive detector, i.e. a ${}^6\text{LiF/ZnS(Cu)}$ scintillator coupled with a Peltier-cooled Andor CCD camera, located behind the sample. The spatial resolution (about 330 μm) of the imaging system was limited by the divergence of the neutron beam ($L/D = 233$). To compensate for the spatial inhomogeneity of the beam and internal scintillation effects, the raw two-dimensional digital image was normalized (see Fig. 2.) both with the open beam profile recorded in the absence of the sample and with the dark image recorded with closed neutron beam.

Results and discussion

Bulk and surface composition

PGAA results verified that the coins contain 96 weight% platinum, minor amounts of Ir and Fe and further Cu and Rh content below 1 weight% quantity. With the off-line counting measurements, besides the decay gamma-lines of ${}^{199}\text{Pt}$ ($T_{1/2}=31$ minutes) and ${}^{194}\text{Ir}$ ($T_{1/2}=19.3$ hours), the off-line counting measurements detected ${}^{198}\text{Au}$ ($T_{1/2}=2.7$ days) and ${}^{56}\text{Mn}$ (2.6 hours), as well as ${}^{104}\text{Rh}$ ($T_{1/2}=42$ seconds). The amount of the elements could be determined relative to the calculated mass of Pt. Concentration of iridium was determined with 2.3–2.8 weight% uncertainty at the most precise level, while gold and manganese were of higher uncertainty due to their low quantity. Though the presence of iridium was also determined with the PGAA method, the uncertainty of these results was rather high, thus we listed the concentration values of iridium based on the off-line counting measurements. Because of the short half-life of the ${}^{104}\text{Rh}$ radionuclide, the exact quantity of Rh could not be determined from the off-line counting measurement, however its presence was indicated. Table 1 summarizes the PGAA results. Note that the Pt and Fe results of coin 1837 and 1838 agree within (1σ) uncertainty

margin. The iridium content in the coin issued in 1838 is 15 weight% higher than in the coin issued in 1837, while the amount of the other elements is slightly less.

With PIXE, the following elements were detected: Pt, Fe, Ir, Cu, Mn, Au, V and Ni (**Table 2.**). The results indicated 5–10% and 10–30% relative internal concentration difference among the multiple analysed surface areas for each coin in the Ir and Cu content, respectively. The concentration difference in case of the other detected elements exceeds 50% relative of the analysed values, at several parts. These results are in agreement with the previous findings, i.e. the coins are spatially heterogeneous on the scale of 1–2 mm diameter areas (Rehren et al. 2012; Weerd et al. 2004).

Both the previous study (Rehren et al. 2012) and one of the PIXE results indicated the presence of elevated gold content on the reverse side of the Pt 3-Rubel coin from 1838. Using bulk PGAA and off-line counting measurement, more than fifty times less gold content (70–100 µg/g) was detected than the highest local concentration identified with PIXE (5300 µg/g). This confirms that the gold specks/inclusions (if present) are rare and unevenly distributed within the coins. This is even more characteristic of the amount of iron on the surface, which varies by up to ten times between the different measurement points with PIXE.

Based on earlier studies, the platinum content in its native ores rarely exceeds 80 weight% (Rehren et al. 2012). In a recent study Kuttyrev et al. (2021) examined platinum-group minerals in Ural-Alaskan type complexes. They found that the Matysken complex contains the most common Pt-bearing mineral, isoferroplatinum (Fe₃Pt) in mm-scale nuggets, as well as a wide range of PGE, Fe and Cu alloys, sulfarsenides and antimonides, which

formed in serpentine veinlets together with awaruite (Ni₃Fe) and base metal sulfides. In their Supplementary Table S4 (Kuttyrev et al. 2021) the authors summarised the typical chemical compositions of different isoferroplatinum minerals and Ni₂FePt analyzed by inductively coupled plasma mass spectrometry (ICP-MS) and atom-emission spectroscopy combined with wet chemistry.

Table 1.: Bulk elemental composition of the platinum coins obtained using PGAA and off-line counting measurements. The concentrations are listed in weight percent unit together with their relative uncertainty (Rel. unc. (%)). The elements marked with asterisk were determined from the off-line counting measurements.

1. táblázat: A platina érmék PGAA módszerrel és off-line gamma spektrometriával meghatározott térfogati átlagösszetétele. A koncentrációkat tömegszázalékban adtuk meg, mérési bizonytalanságukkal együtt (Rel. unc. (%)). A csillaggal jelölt elemeket az off-line gamma spektroszkópiai mérések segítségével sikerült meghatározni.

Element	Coin 1837		Coin 1838	
	Weight %	Rel.unc. (%)	Weight %	Rel.unc. (%)
Pt	96	0.5	96	0.5
Fe	1.3	8	1.4	8
Ir*	1.17	2.3	1.35	2.8
Cu	0.49	3.8	0.19	3.8
Mn*	0.0014	12	0.0008	17
Au*	0.010	16	0.007	15
Rh	0.14	6	0.12	6

Table 2: PIXE results in weight percent concentration

2. táblázat: PIXE módszerrel meghatározott tömegszázalékos összetétel

	PIXE measurement	filter	Elements in weight percent concentration							V (ppm)
			Pt	Fe	Ir	Cu	Mn	Au	Ni	
Coin 1837	#1 reverse	60 µm PC	96.7	1.12	1.61	0.49	0.024		0.044	
	#2 reverse	100 µm Al	97.6	0.18	1.81	0.38			0.030	26
	#3 cross section	60 µm PC	96.5	1.47	1.49	0.47			0.077	85
	#4 cross section	100 µm Al	95.6	1.13	1.65	0.41			0.084	
Coin 1838	#1 reverse	100 µm Al	97.0	0.94	1.32	0.38	0.035		0.064	
	#2 reverse	60 µm PC	97.0	1.30	1.29	0.36	0.024		0.039	177
	#3 reverse	100 µm Al	97.7	0.14	1.42	0.22	0.0017	0.53	0.021	

According to their data, the typical Pt content of isoferroplatinum is 62–90 weight%, Fe varies between 8 and 30 weight%, Cu varies between 0.2–3 weight%, and Ir ranges from 0.07–3.5 weight%, while the maximum detected amounts of Ni and Rh were 3 and 1.7 weight%, respectively.

In Ni₂FePt the following concentrations were detected: 11–32 weight% Pt, 24–34 weight% Fe, 39–53 weight% Ni, 0.1–4.6 weight% Cu, and 0.02–0.15 weight% Rh. Although osmium, ruthenium and palladium were also detected in some instances, these are not discussed here, because their quantities were under the detection limit of our applied analytical techniques, PGAA and PIXE. Manganese and gold were detected with PGAA and PIXE, too, but we have no comparative data for them from the geological study. Both elements show high concentration differences in the surface and in the bulk.

In **Table 3.** the PGAA and PIXE data are compared to draw conclusions on the heterogeneity of the coins. Apart from platinum, all elements are unevenly distributed within the coin volumes. Significantly, the iron concentration measured with PIXE on the cross section of the cut coin shows good agreement with its bulk PGAA data. On the surface, however, its quantity is often only one tenth of that measured in the total volume. The

iridium concentration of coin 1837 measured with PIXE is 30–50% relative higher than that obtained with PGAA, suggesting that iridium is enriched on the surface, while the surface-to-bulk iridium content in coin 1838 agrees within 2% relative of the absolute value, suggesting a more uniform distribution in the whole volume.

The almost completely depleted amount of Fe and Ni in the coins compared to the composition of the native Pt-containing minerals proves the mastery of large-scale routine platinum refining and the development in the first decades of the nineteenth century. The reduction in the contents of Ir and Ru in the coins, to around 1 weight% and 0.5 weight%, respectively, is less pronounced when using the raw mineral data from Kuttyrev et al. (2021) for pure isoferroplatinum nuggets as a baseline; however, bulk Russian platinum ore concentrate data provided by Rainer (1902, 15) indicate an iridium content of more than 4 weight%, but only 0.3 weight% ruthenium. As it is likely that the large-scale processing in St Petersburg would have been based on panned ore concentrates of mixed mineralogy rather than pure isoferroplatinum, it is reasonable to conclude that also the separation of platinum from its main PGE companion iridium had made good progress by the time the coins were produced, despite the significant residual amounts left in the coins analysed here.

Coin 1837	Pt	Fe	Ir	Cu	Mn
PGAA min	95.5	1.2	1.14	0.47	0.0012
PIXE min	95.6	0.18	1.49	0.38	0
PGAA max	96.5	1.4	1.20	0.51	0.0016
PIXE max	96.7	1.47	1.81	0.49	0.024
PIXE/PGAA min	<i>1.00</i>	<i>0.15</i>	<i>1.31</i>	<i>0.81</i>	<i>0.00</i>
PIXE/PGAA max	<i>1.00</i>	<i>1.05</i>	<i>1.51</i>	<i>0.96</i>	<i>15.00</i>
Coin 1838	Pt	Fe	Ir	Cu	Mn
PGAA min	95.5	1.3	1.31	0.183	0.00066
PIXE min	97.0	0.14	1.29	0.22	0.0017
PGAA max	96.5	1.5	1.39	0.197	0.00074
PIXE max	97.7	1.3	1.42	0.38	0.035
PIXE/PGAA min	<i>1.02</i>	<i>0.11</i>	<i>0.98</i>	<i>1.20</i>	<i>2.58</i>
PIXE/PGAA max	<i>1.01</i>	<i>0.87</i>	<i>1.02</i>	<i>1.93</i>	<i>47.30</i>

Table 3.:
Comparison of surface and bulk compositions, in weight percent

3. táblázat:
Felszíni és térfogati összetétel eredmények összehasonlítása, tömegszázalékban megadva

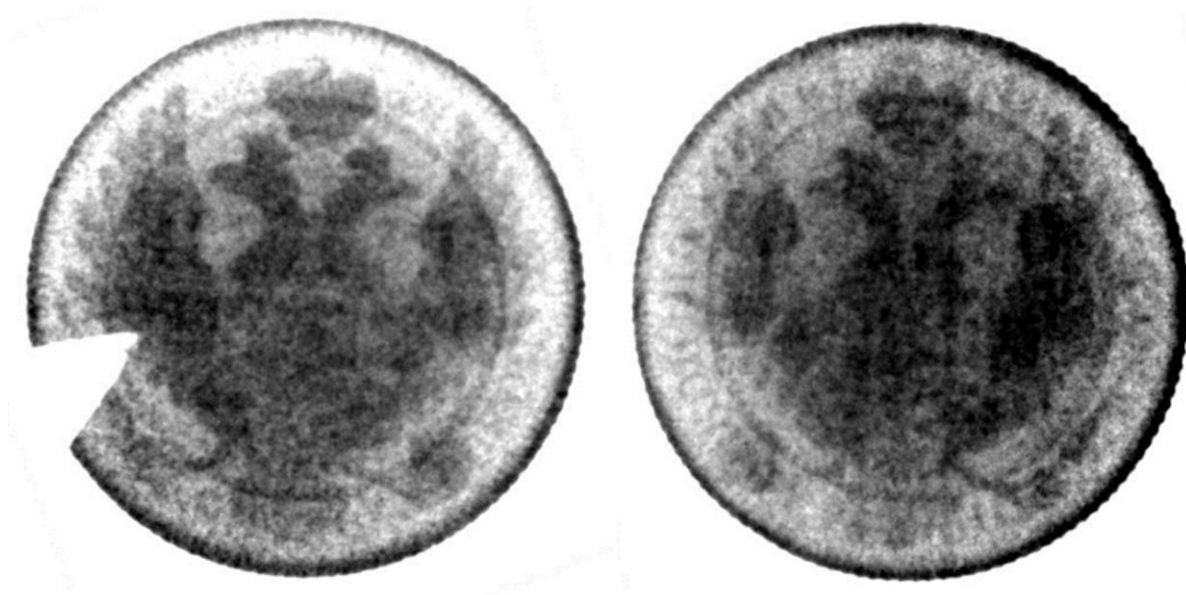


Fig. 2.: Neutron radiography of the platinum coins issued in 1837 (left) and 1838 (right)

2. ábra: 1837-es (bal) és 1838-as évből (jobb) származó platina érmékről készült neutron radiográfia

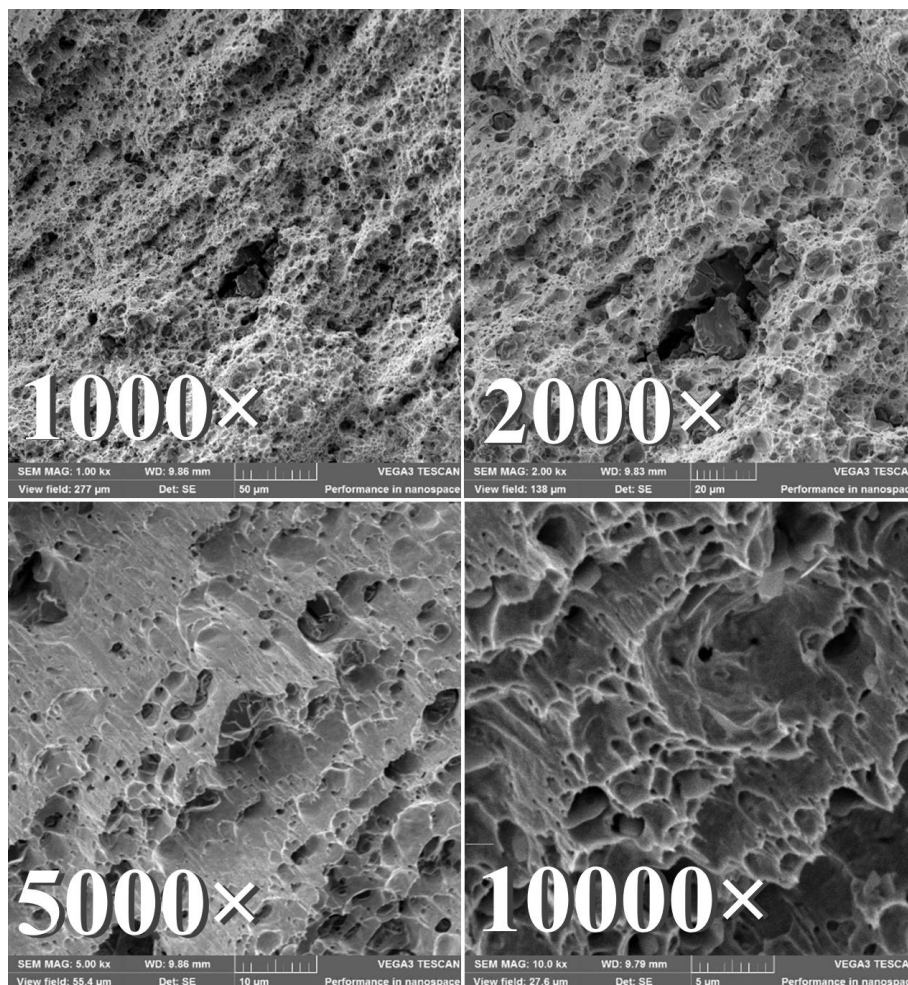


Fig. 3:
SEM pictures for a small piece fracture surface from the Pt coin issued in 1837

3. ábra:
Az 1837-es platina érméből kivágott darab törési felszínének pásztázó elektronmikroszkópos képe

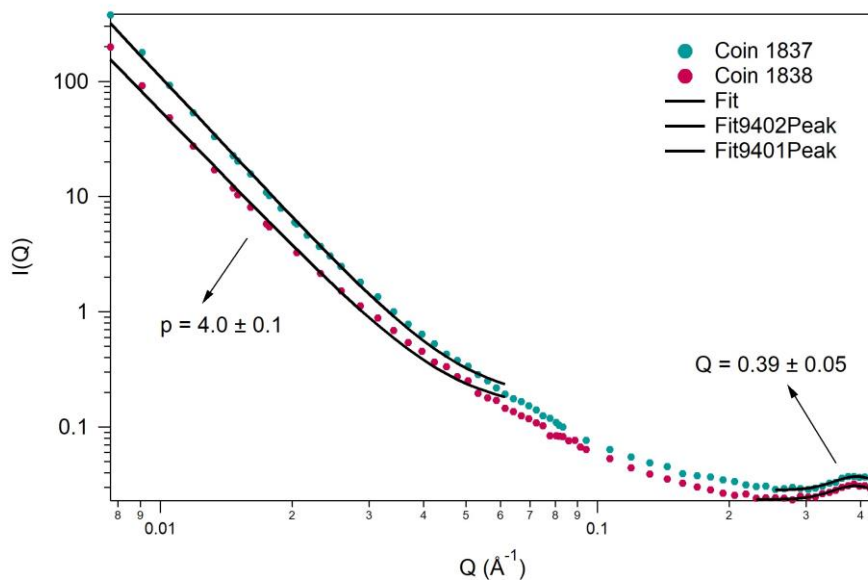


Fig. 4.:
Radially averaged intensities as a function of the scattering vector, with the fitting curves and parameters

4. ábra:
Radiálisan átlagolt intenzitások a szórásvektor függvényében, az illesztési görbékkel és paraméterekkel

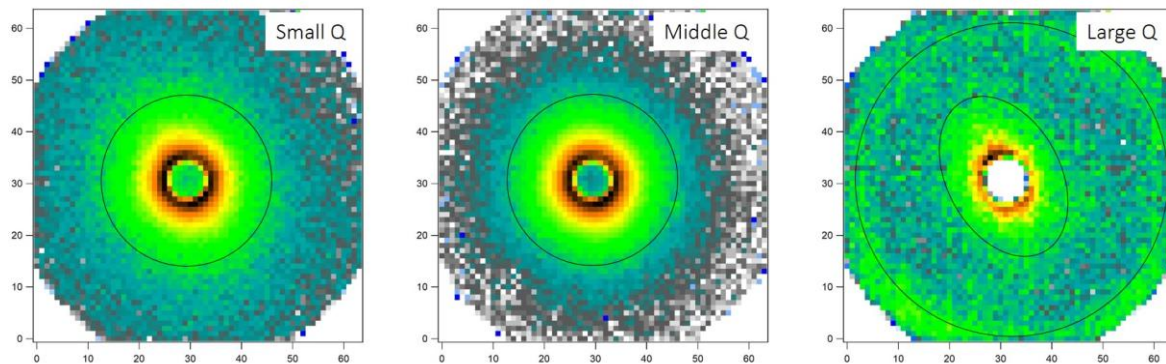


Fig. 5: 2D scattering images of the coin issued in 1837 measured at different scattering vector ranges

5. ábra: Az 1837-ben kiadott pénzérme 2D képei szórásképei különböző szórásvektor tartományokon mérve

Macro- and microscopic structure

The neutron radiography revealed no macroscopic heterogeneity. The darker areas correspond to thicker parts of the coins (see **Fig. 2.**), reflecting the engravings in the dies used for striking the coins. No other heterogeneities in NR transparency were observed.

SEM images were taken from a fractured piece of the coin issued in 1837. The used SEM instrument was a VEGA3 TESCAN scanning electron microscope. The images show generally homogeneous structure with inclusions already visible by 1000× magnification (**Fig. 3.**).

Nanostructure

The nanostructure of both studied coins showed similar SANS curve shapes, and the model fitting parameters were also similar (**Fig. 4.**). From the scattering in the high- and middle-Q range (**Fig. 5.**),

power-law exponents of 4.06 ± 0.05 and 3.91 ± 0.05 were calculated, which are characteristic of smooth interfaces. In the present case, the interfaces are attributed to grain boundaries with sizes larger than 100 nm (100 nm being the upper size limit of the YS-SANS). Smooth grain boundaries indicate a homogeneous microstructure, as precipitates or other second phase separations would reduce the value of the power-law exponent.

At the Q value of 0.39 \AA^{-1} , a small peak was observed, corresponding to a real-space size of $Q/2\pi = 16 \text{ \AA}$. This peak is believed to originate from very small scattering domains (pores, cracks) whose small-angle scattering is at the detection limit of the instrument. Additionally, these domains exhibit a certain directionality, which cannot be detected in the middle and high Q ranges. This suggests that a possible directional fingerprint of the production remains in the sample at the level of the smallest entities.

TOF-ND data did not provide clear results on the presence of iron-oxides, therefore it is not reported here in more detail.

Conclusion

In this study the suitability and potential of neutron-based methods were explored for the analysis of minor and trace impurities as well as structural features at several size scales within two Russian platinum coins. The surface and bulk compositions were determined using PIXE and PGAA techniques, respectively. By comparing the results of the surface and bulk analytical techniques, it can be concluded that the impurities, primarily iron, iridium, gold, copper, and manganese are unevenly distributed within the platinum coins. Particularly for iron and copper a systematic higher concentration was found in the body of the coins compared to their surfaces, which likely reflects the bleaching of the coins after their hot treatment to remove surface contaminants, such as iron oxide scales or inclusions that would diminish the silvery shine of the fresh coins. However, in the case of the coin issued in 1838 the surface and bulk iridium concentrations showed good agreement, implying its more homogeneous distribution compared to the coin from 1837. Small-angle neutron scattering studies confirmed the homogeneous microstructure of the coins, while a possible residual directional fingerprint of the production technique was observed in the smallest size range.

The underlying historical research question that triggered this study relates to the potential of these coins to document the development of platinum metallurgy in the first half of the 19th century. During this period, significant advances were made in the metallurgy and chemistry of the platinum group elements, and in the metal refining and processing at the mint in St. Petersburg. Some of these advances and changes in process may be reflected in the coins' composition, issued over 14 years, from 1828 to 1842. Based on the research presented here, PGAA analysis together with off-line counting of a large set of coins, including multiple coins from each year, is the most promising approach to unlock this archive of this specific chapter in the history of science and technology related to platinum metallurgy.

Contribution of authors

Maróti Boglárka Validation, Investigation, Visualization, Writing – Review & Editing. **Kasztovszky Zsolt** Investigation, Writing – Review & Editing, Project administration. **Len Adél** Validation, Investigation, Visualization, Writing – Review & Editing. **Kis Zoltán** Investigation, Visualization, Writing – Review & Editing. **Káli György** Investigation. **Füzi János†** Validation, Investigation.

Kovács Imre Validation, Investigation, Visualization, Writing – Review & Editing. **Szentmiklósi László** Validation, Investigation. **Szökefalvi-Nagy Zoltán** Validation, Investigation, Writing – Review & Editing. **Rosta László** Funding acquisition. **Thilo Rehren** Conceptualization, Investigation, Supervision, Resources, Writing – Original Draft, Review & Editing.

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